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ION-EXCHANGE SEPARATIONS ON MIXED COLUMNS

TAKEO YAMABE

Institute of Industrial Science, University of Tokyo, Minato-ku, Tokyo (Japan)

SUMMARY

The separation of metal ions by elution with a solution containing a chelate-forming agent, namely an organic hydroxy acid (lactic acid or tartaric acid) was investigated by changing the mixing ratio (γ) of the cation- and anion-exchange resins and by changing the pH of the eluent. When the concentration of lactic acid was 0.5 M at pH 2.8 and $\gamma = ^1/_2$, a mixed sample of Lu, Tm, Er, Ho, Dy, Tb and Gd was completely separated within 100 min. When the concentration of tartaric acid was 0.25 M at pH 3.0 and $\gamma = 2$, a mixed sample of Cu, Zn, Pb, Co and Cd was completely separated within 90 min.

INTRODUCTION

In place of single columns which contain either a cation- or an anion-exchange resin, we succeeded in achieving ion-exchange separations on mixed columns which contained both cation- and anion-exchange resins. It was found that the mixed columns were particularly useful when the species to be separated were amphoteric electrolytes or had complex-forming properties with the eluents. In this paper, we discuss the separation of metal ions by elution with a solution containing a chelate-forming agent, namely an organic hydroxy acid.

Separations by mixed column ion-exchange chromatography
In 1964[1], we studied mixed column ion-exchange chromatography for the first time. The elution of Cu(II) and Fe(III) with hydrochloric acid was studied, and the equation of the distribution ratio was derived for the mixed column.

In 1968[2], we studied the group separation of amino acids on a mixed ion-exchange column as a model for amphoteric electrolytes. The resins used were weakly acidic (Amberlite CG-50) and weakly basic (Amberlite CG-4B), NaCl solution was used as the eluent and the representative amino acids used were glycine (neutral), aspartic acid (acidic) and histidine (basic). On the cation-exchange column, glycine and aspartic acid were not separated, and on the anion-exchange column, glycine and histidine were not separated. On the mixed column with 0.05 N NaCl as eluent, however, the three amino acids were eluted in the order glycine, aspartic acid and histidine.

We then directed our interest to the separation of the transition metals. We

used 0.5 N hydrochloric acid as eluent, and Cu, Zn and Cd were separated on a mixed column (cation:anion mixing ratio = 1:1)[3]. However, with HCl as eluent, high performance could not be obtained, and organic hydroxy acids were used in subsequent experiments.

THEORETICAL

Elution behaviour of metal ions

In ion-exchange chromatography, the following equation is obtained:

$$V_m = V_s + \bar{K}_d \cdot V_R \tag{1}$$

where V_m is the peak volume or retention volume (ml), V_s the volume (ml) of interstitial water, V_R the resin volume (ml) and $\bar{K}_d$ the distribution coefficient during column operation, which is almost equal to the distribution coefficient, K_d, at equilibrium. Under the actual operating conditions, K_d is replaced by K_d^M, the distribution ratio.

If the flow-rate is constant, V_m, V_s and V_R are replaced by t_m, t_s and t_R, respectively. Accordingly, t_m is the retention time.

Distribution ratio in the mixed column[4]

The distribution ratio, K_d^M, for the total species in the mixed column can be described as follows[1]:

$$K_d^M = \frac{V_R^+ \cdot K_d^+ + V_R^- \cdot K_d^-}{V_R} \tag{2}$$

where the distribution ratios for the cations and anions are K_d^+ and K_d^-, respectively, the volumes of the cation- and anion-exchange resins are V_R^+ and V_R^-, respectively, and the total volume of the resins is V_R.
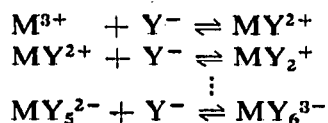
An organic hydroxy acid, the chelating agent, is weakly acidic and we can consider only the first degree of dissociation. Organic acids dissociate as follows:

$$HY \rightleftharpoons H^+ + Y^-$$

and the dissociation constant, K_a, is

$$K_a = \frac{[H^+]\,[Y^-]}{[HY]} \tag{3}$$

The equilibria in the process forming a complex between a metal ion M^{3+} (for example, a rare earth metal ion) and Y^- are:

$$M^{3+} + Y^- \rightleftharpoons MY^{2+}$$
$$MY^{2+} + Y^- \rightleftharpoons MY_2^+$$
$$\vdots$$
$$MY_5^{2-} + Y^- \rightleftharpoons MY_6^{3-}$$

However, for simplicity, it is assumed that only M^{3+}, MY_3 and MY_6^{3-} are present, and then the successive stability constants, k_1 and k_2, are obtained:

$$k_1 = \frac{[MY_3]}{[M^{3+}]\,[Y^-]^3} \tag{4}$$

$$k_2 = \frac{[MY_6^{3-}]}{[MY_3]\,[Y^-]^3} \tag{5}$$

If the total concentrations of organic hydroxy acid and metal ion are C_Y and C_M, respectively, then

$$C_Y = [Y^-] + [HY] \tag{6}$$

$$[Y^-] = C_Y \cdot \frac{K_a}{K_a + [H^+]} \tag{7}$$

$$C_M = [M^{3+}] + [MY_3] + [MY_6{}^{3-}] \tag{8}$$

Therefore,

$$K_d{}^+ = \frac{[M^{3+}]}{C_M} \cdot K_d{}^{0+} (M^{3+}) = \frac{1}{1 + k_1 [Y^-]^3 + k_1 k_2 [Y^-]^6} \cdot K_d{}^{0+}(M^{3+}) \tag{9}$$

$$K_d{}^- = \frac{[MY_6{}^{3-}]}{C_M} \cdot K_d{}^{0-} (MY_6{}^{3-})$$

$$= \frac{k_1 k_2 [Y^-]^6}{1 + k_1 [Y^-]^3 + k_1 k_2 [Y^-]^6} \cdot K_d{}^{0-} (MY_6{}^{3-}) \tag{10}$$

where $K_d{}^{0+}$ and $K_d{}^{0-}$ are the values when chelating agent does not exist in the column.

The distribution ratio, $K_d{}^M$, in the mixed column, therefore, can be described as follows:

$$K_d{}^M = \frac{1}{V_R} \cdot \frac{V_R{}^+ \cdot K_d{}^{0+} (M^{3+}) + V_R{}^- \cdot k_1 k_2 [Y^-]^6 K_d{}^{0-} (MY_6{}^{3-})}{1 + k_1 [Y^-]^3 + k_1 k_2 [Y^-]^6} \tag{11}$$

As shown in eqn. 11, the distribution ratio, $K_d{}^M$, changes greatly in accordance with the stability constant of the complexes, the pH of the solution phase and the mixing ratio of the ion-exchange resins. Although eqn. 11 shows only three chemical species with respect to the metal M, the effects of MY^{2+}, $MY_2{}^+$, $MY_4{}^-$ and $MY_5{}^-$ on $K_d{}^M$ are also important.

When the pH is increased or $[H^+]$ is decreased, then from eqn. 7 $[Y^-]$ is increased, and therefore $K_d{}^M$ is decreased.

Effect of the mixing ratio on the distribution ratio

We define the mixing ratio, γ, as follows:

$$\gamma = \frac{V_R{}^+}{V_R{}^-} \tag{12}$$

As shown by eqn. 2, the effect of γ on $K_d{}^M$ is influenced most by the values of $K_d{}^+$ and $K_d{}^-$.

The elution behaviour of metal ions falls into three types, according to the difference between $K_d{}^+$ and $K_d{}^-$, as shown in Fig. 1. In Fig. 1[3], each metal ion was eluted separately. In type 1, where the metal is Cu^{2+} and the eluent 0.5 N HCl, $K_d{}^M$ decreases when γ is decreased or $V_R{}^-$ is increased. In type 2, where the metal is Zn^{2+} and the eluent 1 N HCl, $K_d{}^M$ increases when γ is decreased or $V_R{}^-$ is increased. In type 3, where the metal is Zn^{2+} and the eluent 0.5 N HCl, the $K_d{}^M$ values are almost constant for all mixing ratios.

It is considered that in type 1 $K_d{}^+ \gg K_d{}^-$, in type 2 $K_d{}^+ \ll K_d{}^-$, and in type 3, $K_d{}^+ \approx K_d{}^-$.
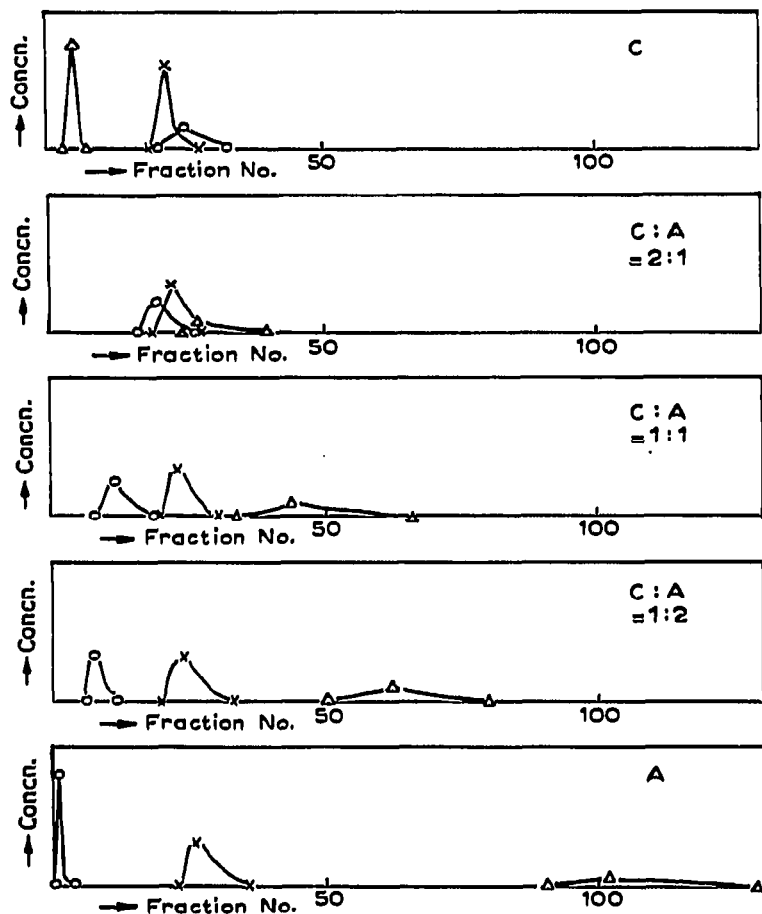
Fig. 1. Typical elution behaviour of metal ions on mixed columns. $\bigcirc$, Cu^{2+} (0.5 N HCl); $\triangle$, Zn^{2+} (1 N HCl); $\times$, Zn^{2+} (0.5 N HCl). C:A = cationic:anionic ratio. One fraction = 14 ml.

The effect of γ on K_d^M is different from the effect of pH on K_d^M. While the increase in pH always causes a decrease in K_d^M, the decrease in γ results in different effects in types 1, 2 and 3. The combination of various mixing ratios and pHs will therefore make very difficult separations possible in practice.

EXPERIMENTAL

Preparation of mixed columns

The cation- and anion-exchange resins used were strongly acidic and strongly basic (Diaion SK and SA, 25 μm, respectively), and were conditioned with hydrochloric acid and sodium hydroxide solution in the usual manner. After conditioning, appropriate amounts of the resins were mixed in a concentrated electrolyte solution, such as 20% sodium chloride solution, so as to avoid violent aggregation in pure water.

Column operation and determination of metal ions

The total amount of the resins in the column was about 4 ml and the height of the resin in the 5-mm I.D. column was 200 mm. A 0.5-ml volume of each of 2×10^{-3} M solutions of the metal ions or mixed ions was added to the upper part of the column and then developed with an eluent at an elution-rate of 60 ml/h (except for the separation of Lu, Yb and Tm, which was carried out at an elution-rate of 30 ml/h). Throughout the rare earth separations, the mixing ratio in the mixed column was maintained at $\gamma = {}^1/_2$.

The eluent for the separation of the heavy rare earth elements was 0.5 M lactic acid and 0.06 M NaCl at pH 2.8, adjusted with NaOH, and the same for the separation of Lu, Yb and Tm except that the pH was 2.63. The eluent for the separation of the light rare earth elements contained the same components, except for different pHs of 2.8, 2.9, 3.0 and 3.1. The eluent for the separation of typical transition metals (except for Pb) was 0.25 M tartaric acid and 0.07 M NaCl at pH 3.0.

The concentration of each metal ion was determined coulometrically with a Hitachi coulometric monitor, Type 030. The principle of this instrument involves the coulometry of Hg ions isolated by the reaction of metal ions with the EDTA complex of Hg, and therefore the identification of the peak is carried out by comparison with the elution of single metal ions.

RESULTS AND DISCUSSION

Separation of rare earth elements[4]

Figs. 2 and 3 show separations of the rare earth elements. In the upper part of Fig. 2 is shown the separation of heavy rare earth elements (excluding Yb), Lu, Tm, Er, Ho, Dy, Tb and Gd at pH 2.8 and $\gamma = {}^1/_2$, and in the lower part of Fig. 2 is shown the separation of Lu, Yb and Tm at pH 2.63 and $\gamma = {}^1/_2$.
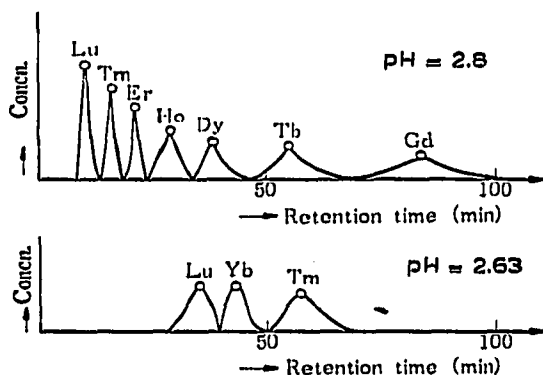

Fig. 2. Separation of heavy rare earth elements on mixed columns. Eluent: lactic acid. C:A = 1:2.

In the case of the single column of anion-exchange resin, all of the elements were eluted immediately, and in the case of the single column of cation-exchange resin, too large elution volumes were estimated. As shown in Fig. 2, the elements were completely separated within 100 min.

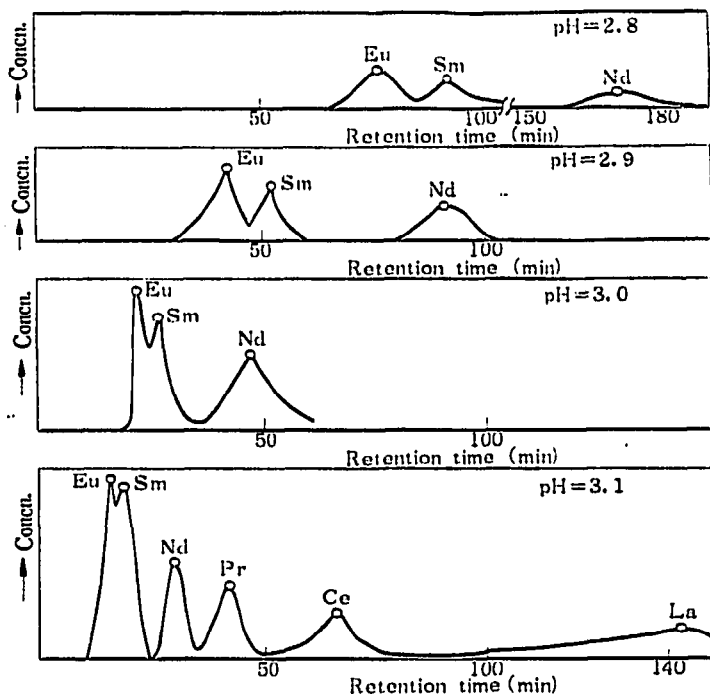In the separation of light rare earth elements, we examined the relationship

Fig. 3. Relationship between pH and elution behaviour in light rare earth elements. Eluent: lactic acid. C:A = 1:2.

between pH and elution behaviour. When the pH is increased, the retention time of each element is remarkably shortened. A mixed sample of Eu, Sm, Nd, Pr, Ce and La was completely separated within 140 min, except for Eu and Sm.

Separation of typical transition elements

In Fig. 4, the relationship between the mixing ratio and elution behaviour for typical transition metals (except Pb) is shown with the eluent being 0.25 M tartaric acid at pH 3.0. Zn, Pb and Co showed type 1, Cd type 2 and Cu type 3 elution behaviour.

The best result was obtained at $\gamma = 2$, and a mixed sample of Cu, Zn, Pb, Co and Cd was completely separated within 90 min. When cation-exchange resin was used, Pb and Cd were not separated, and if γ was less than 2, the separation of Cu, Zn, Pb and Co gradually became more difficult. On the anion-exchange resin, the peak of Cu occurred only as a shoulder.

CONCLUSION

When the concentration of eluent was fixed, the most favourable conditions for separation were obtained by changing the mixing ratio (γ) of the cation- and anion-exchange resins or by changing the pH of the eluent.

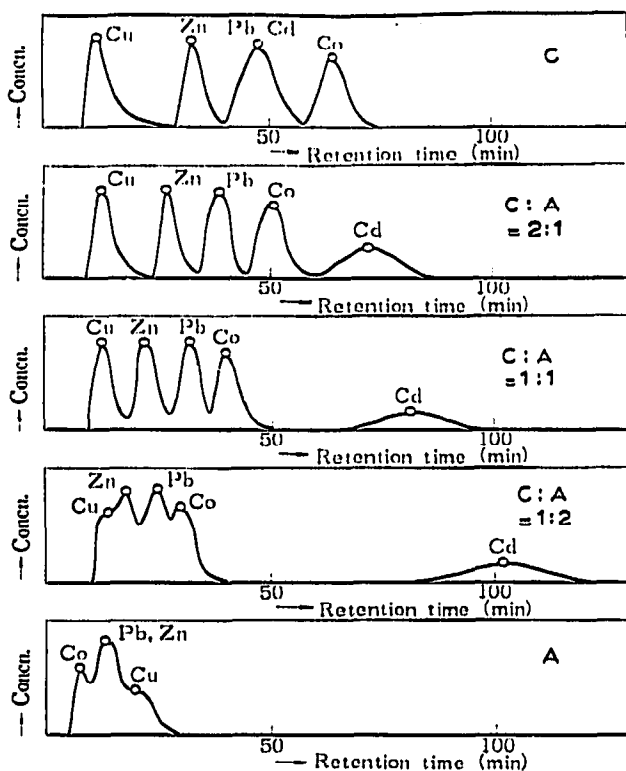There are three types of elution behaviour with respect to the change of γ.

Fig. 4. Relationship between mixing ratio and elution behaviour in typical transition metals. Eluent: tartaric acid.

When γ is decreased, the retention volume will increase, decrease or remain constant in accordance with these types of behaviour.

When the concentration of lactic acid was 0.5 M at pH 2.8 and $\gamma = \frac{1}{2}$, a mixed sample of Lu, Tm, Er, Ho, Dy, Tb and Gd was completely separated within 100 min.

When the concentration of tartaric acid was 0.25 M at pH 3.0 and $\gamma = 2$, a mixed sample of Cu, Zn, Pb, Co and Cd was completely separated within 90 min.

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